

SCIENCE

VOL. 102

FRIDAY, DECEMBER 7, 1945

No. 2658

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SCIENCE: A Weekly Journal, since 1900 the official organ of the American Association for the Advancement of Science. Published by the American Association for the Advancement of Science every Friday at Lancaster, Pennsylvania.

Editors: JOSEPHINE OWEN CATTELL and JAMES CATTELL.

Policy Committee: MALCOLM H. SOULE, ROGER ADAMS and WALTER R. MILES.

Advertising Manager: THEO. J. CHRISTENSEN.

Communications relative to articles offered for publication should be addressed to Editors of Science, The Science Press, Lancaster, Pa.

Communications relative to advertising should be addressed to THEO. CHRISTENSEN, Advertising Manager, American University, 3801 Nebraska Ave., NW, Washington 16, D. C.

Communications relative to membership in the Association and to all matters of business of the Association should be addressed to the Permanent Secretary, A.A.A.S., Smithsonian Institution Building, Washington 25, D. C.

Annual subscription, \$6.00

Single copies, 15 cents

THE BASIC MECHANISMS OF STATIC ELECTRIFICATION

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THE term "static electrification," as here used, covers all processes for producing segregation of positive and negative electrical charges by mechanical actions which operate by contact or impact between solid surfaces, between solid and liquid surfaces, or in the rupture of solid or liquid surfaces by gases. These involve such phenomena as frictional electrification, spray electrification, electrification in dust storms, etc. A review of these phenomena in general shows a most unsatisfactory array of discordant, often non-reproducible and confusing results, whose theoretical interpretation in some cases is quite hopeless.^{1,2,3,4,5}

¹ H. F. Richards, *Phys. Rev.*, 22: 122, 1923; and 16: 290, 1920.

² Cardani, *N. Cimento*, 23: 199, 1922; Jones, *Phil. Mag.*, 29: 272, 1915; Owen, *Phil. Mag.*, 17: 457, 1909; E. Perruca, *N. Cimento*, 22: 56, 1921.

³ Cohn, *Ann. de Phys.*, 30: 777, 1909, and 43: 1048, 1914.

⁴ Ulrey, *Phys. Rev.*, 12: 47, 1918.

⁵ P. E. Shaw and C. S. Jex, *Proc. Roy. Soc. London*,

It is believed that in a considerable measure this situation results from the fact that many investigators are not alert to the possibility that in any one aspect of their studies not one but perhaps two or more of the various basic mechanisms may have been active. Such complications make theoretical interpretation in terms of any single proposed mechanism most difficult. In order to clarify the situation it is proposed to list the known mechanisms and briefly to discuss them. The basic mechanisms active are:

(1) Electrolytic effects, caused by distribution of electrolytic ions in solutions of liquids of high dielectric constants between the solutions and metals or solids, on contact, followed by mechanical separation. Since diffusion of ions across interfaces build up considerable potentials,

A118: 97, 1928; A. Fleming, *Proc. Roy. Soc. London*, 53: 51, 1941; R. Schuurman, *Proc. Phys. Soc. London*, 53: 547, 1941; F. Boning, *Zeits. f. Tech. Physik*, 8: 385, 1927; H. Israel, *Zeits. f. Tech. Physik*, 9: 289, 1928.

heavy electrification may occur. These effects are well known but may appear in unusual connections.

(2) Contact or Volta electrification between clean, dry metallic surfaces or surfaces of metallic conductors and of semi-conductors. These phenomena are well known in the theory of the metallic state and involve movements of *free electrons* across metallic potential barriers as a result of differences in the work function of the metal surfaces.

(3) Spray electrification, produced by the disruption of surface films of liquids and solutions by mechanical forces such as the atomizing and bubbling of liquids and perhaps the shattering of liquid jets of high velocity by solid surfaces.

(4) Frictional or tribo electrification, as a result of impacts or contact and subsequent separation between *dry* non-metallic solid surfaces. This phenomenon is connected with the theory of the solid state and probably depends on transfer of *ions, not electrons*, between lattices of solids. It may involve polarization by pressure and mechanical rupture of polarized units by mechanical forces.¹

(5) Effects by which ions and electrons, created by electrical phenomena in gases or in flames, are segregated and separated by mechanical forces, with or without the presence of electrical fields, produced by mass motions of gases or solids. Examples of these phenomena in processes such as the electrical segregations in flames in exhaust gases from flues, and in the Van de Graaf static generator are well known.

(1) *The Electrolytic Mechanisms.* One of the original theories of contact electrification between solids assumed that *all* such action was electrolytic in nature and involved thin aqueous films on surfaces. However, studies of phenomena with really dry surfaces indicated that contact electrification was more complex and that mechanisms (2) and (4) both produced static electrification which were *not electrolytic*. That any liquid of high dielectric constant will engage in exchange of ions in contact with metals and solid surfaces is, however, well known, and where contact electrification involves the possibility of such exchanges the phenomenon must be analyzed, considering such possibility. It is necessary, therefore, to consider the role of mechanism (1) in all phenomena involving contact between such liquids and surfaces, flow of such liquids over surfaces³ and in impact of liquids against surfaces resulting in electrified sprays.⁶ Consideration of such actions indicates the need of much more work. It may clarify some of the following obscure phenomena. The writer in some unpublished work observed electrification of an insulated section of copper tube when kerosene, an inert hydrocarbon mixture, was allowed to flow through it. It was found that when this kerosene was clean and *dry* there was no charging. Again S. Chapman⁷

studied the charges of droplets of atomized liquids by means of the Millikan oil drop method. He observed that drops with radii of 10^{-5} to 10^{-4} cm in atomized dielectric liquids were highly charged, in some cases with as many as 600 electrons. Droplets of both signs of charge increased roughly in a linear fashion with drop radius and increased further with dielectric constant of the liquid. These charges were supposed to result from spray electrification, mechanism (3). Later careful review of the data on spray electrification indicated that such a mechanism could not be expected to lead to droplets with more than a few electrons of charge.⁸ Hence some other mechanisms must have been active. Electrolytic action is a possible factor, although how it leads to both signs of charge is a problem, unless the sprayed liquids came in contact with two different surfaces. It is clear, however, that highly charged particles of this magnitude could be achieved in such actions, since ion concentrations in solution and segregations at surfaces are very high. Again Lenard^{6,9} in his work on spray electrification reported that by far the greatest charge separation with its spray having of the order of 90 per cent. negative carriers came from the shattering of liquid jets by metals. This, together with reputed observations on the charging of airplane structures under impact of water drops, where very heavy charges were observed which changed in magnitude and sign with the surface coating, again points to other phenomena than mechanism (3). Similarly the dangerous static charges in handling of gasoline by pouring between metal containers and filtering it through chamois skin and metals should be studied with mechanism (1) in mind. It is suspected that an electrolytic mechanism, (1), may be playing an important role in electrification in Lenard's and in the airplane observations where drops are shattered by impact against solids.

(2) *The Contact Potential Mechanism.* The contact potential phenomenon has been quite completely investigated, both theoretically and experimentally, on clean, outgassed metal surfaces. In general, the metal with the higher work function W_A will become positive to that with lower work function W_B , so that on separation $V_{AB} = W_A - W_B$. *Electrons* have migrated from metal A to metal B in this process. This phenomenon is thus *electronic* and clearly defined. It presents no difficulties except for the effect of impurities and absorbed gas films on the surfaces, which change the work function. Since even at 10^{-8} mm pressure monomolecular gas films can form in a few minutes, and since gas films may be of different sorts in the same gas, in different pressure regions,

⁶ P. Lenard, *Wied. Ann.*, 46: 584, 1892, and *Ann. der Phys.*, 47: 413, 1915; Busse, *Ann. der Phys.*, 76: 493, 1925.

⁷ S. Chapman, *Physics*, 5: 150, 1934.

⁸ S. Chapman, *Phys. Rev.*, 52: 184, 1937, and *Phys. Rev.*, 54: 520 and 528, 1938.

⁹ Bühl, *Kolloid Zeits.*, 59: 436, 1932.

as Langmuir¹⁰ has shown, reproducible results require that great care be used. The electrical exchanges in contacts between semi-conductors, such as CuO, and metal, are more complicated owing to the complicated electronic level structures in such substances. However, in all cases it is the *electron* which moves across the boundary and causes charging. The effect observed with semi-conductors may be modified by temperature, illumination by light, impurities, etc. In view of the familiarity of these phenomena there has been a tendency to ascribe all solid to solid electrification to electron transfer.¹ This in the past has confused the picture. Recent work by Debeau¹¹ has shown that the phenomena in the case of all but materials possessing free or quasi free electrons is more likely an ionic exchange—even if a metal is one of the solids.

(3) *The Spray Electrification Mechanism.* Spray electrification, or "Wasserfall Elektrizität," as P. Lenard,^{6,9} its earliest investigator, termed it, is a phenomenon which depends on the action of surface forces in dielectric liquids in increasing the concentration of electrons or perhaps of negative ions in the outer surface layers. It appears as if perhaps in 10^4 or 10^5 molecules in the surface of pure water there is one extra electronic charge.^{3,6,8} Thus an electrical double layer exists in these liquids, with the outside negative and the inside positive, which in water is about 2×10^{-6} cm thick. The physical basis for such layers has not been formulated as yet. If the liquid surface is disrupted by atomizing or bubbling, then the finer droplets emerge with a preponderance of negative charges. Larger drops are neutral, or positive and negative in equal amounts. Subsequent evaporation or condensation may alter the size of such charged droplets. S. Chapman has observed several groups of ions of both signs, of different mobilities of a wide range of values in the bubbling and spraying of water, and has tentatively suggested the nature of the various ion groups.⁸ Dissolved salts and other substances alter the effect in pure water, generally reducing the magnitude of the charges and the proportion of faster ions and equalizing the number of slower positive and negative ions.^{6,8,9} Electrolytic ions enter the double layer and alter it. Alcohol and other liquids show similar effects but with less differences in the number of positive and negative ions.⁸ Pure hydrocarbons show little charging, but large positive and negative carriers of small charge are observed,^{7,8} in equal numbers. The charges of the faster ions appear to be of the order of a few electrons. For spray from impact of water jets on metals, Bühl¹¹ quotes Lenard

as reporting that of the order of 90 per cent. of the spray carriers were negative. With bubbling, both Lenard and Chapman find that 75 per cent. of the carriers are negative, while with atomized water the negative ions are present to an extent of about 55 per cent.^{8,9} In metallic liquids Bühl reports that with pure clean Hg its spray is positive.⁹ The sign of the charge is altered by traces of oxide dust. Traces of Zn in the Hg may reverse the sign of charging. From the results quoted it is clear that spray electrification is a definite mechanism in its own right, but that it may be complicated where spraying occurs by electrolytic and other factors. In metals it is complicated by gas layers, oxidation and other effects and requires more study. It is probably one of the most important mechanisms of the electrical separation in thunder showers and may be of some importance in the charging of planes in flight. Both of the above cited phenomena may be affected by other mechanisms, *i.e.*, the thunder storm by the theory proposed by C. T. R. Wilson,¹² which belongs under mechanism (5) and the plane charging by mechanism (1). At present the heavily charged large drops observed by Chapman⁷ with an atomizer can not be reconciled with mechanism (3), where segregations of *many charges of one sign* in small volumes of surfaces are unlikely.

(4) *Frictional or Tribo Electrical Mechanisms.* The most obscure of all static charging phenomena to date are the static charging of dry non-metallic particles by contact between themselves or with metals either on impact or just on contact,⁵ *i.e.*, frictional charging. The control of studies of these phenomena has been most difficult. Leaving aside the possible complications by mechanisms (1), with liquid films, the effect is real and very important.¹ Some progress was made in a recent study of Debeau¹¹ on the electrification of SiO₂ and NaCl in contact with Ni where dry and relatively controllable surfaces could be obtained by baking out with some control of the gas content. It was found that reproducible results could be obtained and that gas films absorbed on the surfaces radically altered the charges observed. These changed with the gas pressure and nature of the gas. Thus H₂ and H₂O on Ni led to very confusing results while dry N₂, air and O₂ gave consistent results. Films on one, or both, metal and solid having two entirely different absorption isotherms¹⁰ were active. The loss of the one film, perhaps the outer film, leading to inactive surfaces while the loss of the second, perhaps inner film, again increased the electrification. The charge on SiO₂ was negative, but on rock salt it was positive. The conclusion reached was that

¹⁰ I. Langmuir, *Jour. Am. Chem. Soc.*, 38: 2267, 1916, and 40: 1351, 1918.

¹¹ D. Debeau, *Phys. Rev.*, 66: 9, 1944.

¹² C. T. R. Wilson, *Proc. Phys. Soc. London*, 37: 320, 1929, and *Jour. Franklin Inst.*, 208: 1, 1929.

these effects are closely related with the theory of the solid state, which is yet in its infancy. The charging was believed to be a result of the exchange of *atomic* or *molecular ions* to fill up holes, or to remove excess ions, resulting from holes in the lattices from its surface. Surface films of gases on metals are in some cases in the ionic state, which complicates the picture.

Charging by friction of such complex organic substances as cats' fur, ebonite, sealing wax and glass has its obvious explanation in the possible rupture of long chain polar molecules such as those of fatty acids, etc., which through linkage of polar groups at one end with the contacting surface result in the rupture of the molecules and electrical separations. Again the rupture of strained piezo-electric crystals, or rupture by mechanical means, during pressure induced polarization of other substances could lead to electrification.¹ This whole set of phenomena requires much more work, with care to eliminate the actions of other well-known mechanisms, before it is understood.

(5) The action of the rapid diffusion of electronic carriers causing local separations in space in gases, which can be increased by mechanical means, is too well known to require discussion. There are many examples of such phenomena which do not require discussion here since they do not often confuse results of other static separation studies.

However, it should be considered that where electrical fields by polarization cause segregations of charges in droplets or solids in which mechanical rupture along an axis normal to the field can separate

the polarized charge segregations, can not be ignored in all these investigations. Thus it could be possible that Chapman's⁷ heavy charges on drops produced by atomization of various polarizable liquids may have been caused by the presence of unsuspected fields in the neighborhood of his atomizer. Such an effect of charge segregation with mechanical effects of falling drops in the presence of ions in the air has been invoked by C. T. R. Wilson¹² to explain thunderstorm electrification. The mechanism proposed certainly gives charged droplets. Whether it accounts for most of the electrification in thunder clouds is yet another question. A paper by J. Frenkel¹³ which indicates a third mechanism in the electrification of clouds by mechanical forces has just been received by the writer. In this preferential condensation on negatively charged water nuclei of minute size causes charge segregation by gravitational forces. Its highly suggestive character merits study even if it does not apply to the turbulent regime of thunderstorm generation.

In any case, enough has been said to indicate the need for caution and discrimination in the study of static phenomena as influenced by these causes. It is clear that static electrification is caused by at least five different basic mechanisms, or perhaps six, if we include breaking of pressure or field polarized groups. The realization of this and the considerations of the influence of any of these mechanisms on observed phenomena it is hoped will alert investigators to the possibilities involved and assist in clarifying future and past studies.

THE BIOCHEMISTRY OF MUSCLE TRAINING¹

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OUR researches on the biochemistry of muscle training began with our studies of the metabolism and role of creatine in muscle. This work² showed that during training the creatine in muscle increased. This observation signified to us the possibility that creatine plays a definite functional role in muscle. An investigation³ of the creatine content of divers muscle from many fish demonstrated that muscles which were permanently, that is naturally trained, contain more creatine than muscles that work but little; for example, the muscles of the lateral fins of shark, ruff, etc., contain more creatine than the dorsal

(spinal) muscles. These findings permitted the conclusion that during artificial and natural training muscle becomes rich in creatine. Further experiments^{4,5,6,7,8,9,10,11} showed that muscles in which the work capacity has been increased by training possessed also higher levels of phosphocreatine, carnosine,

¹³ J. Frenkel, *Jour. of Phys., USSR*, 8: 285, 1944.

⁴ B. M. Koldaev and R. Gelman, *Ukrainian Biochem. Jour.*, 9: 35, 1936.

⁵ B. M. Koldaev, *Ukrainian Biochem. Jour.*, 10: 4, 1937.

⁶ M. F. Merezhinski, *Ukrainian Biochem. Jour.*, 9: 25, 1936.

⁷ A. V. Palladin, *Am. Jour. Physiol.*, 90: 1929.

⁸ A. V. Palladin, *Jour. Physiol. U.S.S.R.*, 19: 287, 1935.

⁹ A. V. Palladin, *Advances in Biology* (Russian), 7: 3, 1937.

¹⁰ A. V. Palladin, *Ukrainian Biochem. Jour.*, 17: 7, 1941.

¹¹ D. Z. Ferdman and O. Y. Feinshmidt, *Z. physiol. Chem.*, 183: 261, 1929.

¹ Presented at Stanford University, Biology Seminar, May 31, 1945.

² A. V. Palladin and D. Z. Ferdman, *Z. physiol. Chem.*, 174: 284, 1928.

³ A. V. Palladin and I. D. Ochrimenko, *Ukrainian Biochem. Jour.*, 12: 1938.